QUANTUM THEORY OF ATOMS AND MOLECULES

Problems 1

1. Calculate the energy (in kJ mol^{-1}) of IR and visible photons of wavelengths 2.5 μm and 500 nm respectively. What is the longest wavelength photon which could dissociate O_2 (the molar enthalpy of formation of O atoms is 246.5 kJ mol^{-1})?
2. Calculate the velocity of and electron driven from the surface of potassium (work function 2.26 eV) by incident light of wavelength 350 nm.
3. A Na atom travelling in the $+x$ direction at 600 m/s absorbs a photon of wavelength 590 nm from a laser beam moving in the $-x$ direction. By how much is the velocity of the atom reduced? How many photons are needed to bring the atom to rest, of each photon absorbed is subsequently emitted in a random direction?
4. Through what voltage must electrons, initially at rest, be accelerated if they are to be first order diffracted by an angle of 30º when transmitted through a crystal for which the atomic spacing is 10^{-10} m?

Problems 2

1. Show that the function $\psi = N \sin n\pi x/L$ satisfies the Schrodinger equation for a particle in a 1-D box between $x = 0$ and $x = L$ and calculate the value of the normalisation factor N. Evaluate the probability of finding the particle between $0.4L$ and $0.6L$ when $n = 1$ and when $n = 2$. What would you expect the answer to be for high values of n?
2. Calculate the zero point energy and the energy spacings between the first and second energy levels for (i) and electron in a 1-D box of length 1 nm; (ii) an electron in a 1 nm cubic box; (iii) a He atom in a 1 cm cubic box. For this He atom, calculate the value of the quantum number n_x for which the energy of the atom equals the thermal energy $0.5\ kT$ at 300 K.
3. For a particle of mass m moving in a cubic box of side L, where V is zero inside the box and infinite elsewhere, deduce how many states there are at energies below (a) $10\ h^2 / 8mL^2$; (b) $20\ h^2 / 8mL^2$. Which of the energy levels identified exhibit degeneracy?
4. A simple model for the π electrons in conjugated linear alkenes (ethene, dutadiene, hexatriene etc.) assumes their behaviour approximates to that of a particle-in-a-box of length $(N_c - 1)L$ where N_c (2, 4, 6 etc.) represents the number of C atoms in the chain. The number of electrons is thus also N_c and by the Pauli principle the lowest $N_c/2$ levels will be doubly occupied in the ground state. How will the wavelength of the lowest energy electronic transition associated with the promotion of π electrons to higher energy levels vary with the number of C atoms, N_c , in the chain? Why does the model break down completely at high energies?

Problems 3

1. The total energy E of a particle of mass m moving in a 1-D potential $V(x)$ is $E = p^2 / 2m + V(x)$. By formulating p, V and E as quantum mechanical operators, show that this equation transforms into the 1-D Schrodinger equation. How is the Hamiltonian operator modified if there are two non-interacting particles, of mass m_1 and m_2, with potential energies $V(x_1)$ and $V(x_2)$?
2. What is meant by the statement that " the position and linear momentum operators do not commute". Hence explain the origin of Heisenberg's uncertainty principle relating to the associated observables.
3. Use the operators for position and momentum to write down explicit expressions for the mean values of these quantities for a particle in a box of length L (between $x = 0$ and $x = L$) with a wavefunction $\psi = (2/L)^{1/2} \sin n\pi x/L$. You need not evaluate the integrals arising but use symmetry arguments to deduce what mean values you would expect for these observables.

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Problems 4

1. The vibrational frequencies of H_2^+, D_2 and H_2 are approximately 2322, 3118 and 4400 wavenumbers (cm^{-1}) respectively. Calculate the force constants for these molecules and comment on the relative magnitudes of the values you obtain.
2. For the case of H_2 above, calculate the temperature at which the thermal energy kT equals the excitation energy from the ground to the first excited vibrational states.
3. Calculate the difference between the zero-point energy (in kJ mol^{-1}) of C-H and C-D bond stretches, given a C-H vibrational stretching frequency of 2900 cm^{-1}. Hence explain why C-H bonds react more rapidly than C-D bonds in many organic reactions.
4. Compare the classical and quantum mechanical probability distributions for a simple harmonic oscillator at (a) low quantum numbers; (b) at high quantum numbers.
5. HF has a bond length of 92 pm. Calculate the moment of inertia of the molecule and hence the energy required to excite it from the $J = 0$ to the $J = 1$ energy level. (a) At what temperature does this energy equal the thermal energy kT? (b) At what wavelength could this excitation be induced using electromagnetic radiation?

Problems 5

1. The wavefunction for an electron in the 1s orbital of a 1-electron atom of nuclear charge Z is $(Z^3 / \pi a_0^3)^{1/2} \exp(-Zr/a)$.
    (a) Write down an expression for the radial distribution function $4\pi r^2 \psi^2$ and explain why this function has a different physical interpretation to ψ^2.
    (b) Evaluate the most probable radius at which the electron will be found.
    (c) Evaluate the average electron-nucleus separation.
        (hint: the integral of $r^n \exp(-ar)\,dr$ between 0 and ∞ is $n!/ a^{n+1}$)
    (d) Explain why your answers to (b) and (c) differ from each other.
2. Calculate the value of the orbital angular momentum quantum number l and the permitted values of m_l for a gyroscope with a moment of inertia of 10^{-7} kg m^2 rotating with an angular velocity of 159 radians s^{-1}.
3. Calculate the ionisation energies for the hydrogen and deuterium atoms in cm^{-1}. ($R_\infty = 109737.3$ cm^{-1}).
4. The table below (column (a)) lists the energy of some of the observed transitions in the Balmer Series (visible spectral region) of the emission spectrum of atomic hydrogen.
    (i)   Identify the principal quantum numbers n for the upper and lower states for each of the transitions listed for atomic hydrogen.
    (ii)   The energies of some transitions observed in the <u>absorption spectrum</u> of an unknown one-electron ion (e.g. He^+, Li^{2+}, Be^{3+} etc.) are listed in column (b). Given that these transitions originate from the lowest energy level (it is the absorption spectrum…), suggest an identification of the unknown ion.

(a) Hydrogen (cm^{-1})	(b) Unknown ion (cm^{-1})
15233.2	1646254.1
20564.7	1560886.3
23032.5	1316965.2
24373.1	–

5. Deduce the term symbols for the ground and excited states of sodium produced by exciting the *3s* electron to the *4s*, *4p* and *4d* levels. Which of the excited states can be populated by allowed optical transitions from the ground state?
6. The strong lowest energy transition in the absorption spectrum of sodium appears as a single line, unless viewed at higher resolution when splitting into two lines can be resolved. Explain this behaviour and predict how the magnitude of the splitting will vary as the atomic number of the alkali metal increases.